ATTACHMENT 2

APPENDIX 1

RAMAN SPECTROPHOTOMETER

2-1 BACKGROUND

A nonintrusive method is preferred for segregation of chemical agent identification set (CAIS) items during Rapid Response System operations; such methods reduce the risk of releasing chemical agents and industrial chemicals. In November and December 1993, the Project Manager for Non-Stockpile Chemical Materiel conducted tests at Deseret Chemical Depot (DCD) that determined that a Raman spectrophotometer and fiber optic probe system could successfully segregate chemical agents and industrial chemicals contained in unopened CAIS ampules and bottles. Raman spectra were recorded for 103 CAIS ampules and 4 bottles. The field test data showed that in all cases, phosgene (CG), chloropicrin (PS), and chloroform ($CHCl_3$) were identified by the Raman system, even when the samples exhibited severe degradation. Twenty-nine CAIS ampules were determined to contain PS in $CHCl_3$, and 24 ampules were identified to contain CG. Traces of sulfur mustard (HD) in $CHCl_3$ were identified in three ampules. Eight CAIS ampules were determined to contain traces of lewisite (L) in $CHCl_3$, and 39 ampules were identified to contain $CHCl_3$ with unidentified impurities. $CHCl_3$ in CAIS was originally combined with either 5- or 10-percent agent or 50-percent PS; since PS was readily identified with the Raman spectrophotometer system, the $CHCl_3$ spectrum, in the absence of PS peaks, was used to classify the unknowns as agent/$CHCl_3$ mixtures. Solid chloroacetophenone samples were also identified using the Raman system. The successful results of the field test led to the inclusion of a Raman spectrophotometer and fiber optic probe system in the design of the RRS, and further testing at Edgewood Research, Development and Engineering Center (ERDEC)[1].

Following the field test, 30 CAIS ampules and two CAIS bottles examined at DCD were shipped to ERDEC for additional Raman studies and conventional analyses under laboratory conditions. Analysis of the recovered CAIS samples at ERDEC generally confirmed the DCD results. Three HD in chloroform, five L in chloroform, and two PS in chloroform samples previously identified at DCD were confirmed with Raman techniques and conventional analytical methods. New Raman data recorded at ERDEC verified the presence of CG in one CAIS sample, and impurities at DCD. L was also identified in two of the 14 samples containing chloroform in 14 of 19 CAIS samples previously identified as chloroform with unknown containing chloroform using Raman techniques. Gas chromatography and gas chromatography/mass spectrometry analysis of the 19 chloroform/unknown samples from DCD showed that none contained industrial chemicals: 13 samples contained HD in

[1] ERDEC is an organizational part of the U.S. Army Chemical and Biological Defense Command.

$CHCl_3$, and 6 samples contained L in $CHCl_3$. Of particular significance, the conventional analytical results showed that the Raman system did not misidentify the contents of any of the CAIS ampules at ERDEC. Minimum detection limits for HD and L in $CHCl_3$ were experimentally determined at ERDEC to be approximately 0.5 percent [volume/volume (v/v)] and less than 0.5 percent (v/v), respectively, for the Raman system. Raman spectra of GA-simulant and GA-simulant components were also recorded during the ERDEC test. The successful results of this series of studies confirm the decision to use Raman spectroscopy to segregate the contents of all ampules and bottles that do not have the identity clearly established by original labels. All ampules, regardless of markings will be segregated by using the Raman.

2-2 DESCRIPTION

The RRS Raman spectrophotometer is completely housed in the operations trailer and consists of laser sources, fiber optic probes, sample holders, an imaging spectrograph, a low-noise, cooled charge coupling device (CCD) detection system, a personal computer for data analysis and storage, and a laser printer. Both an air-cooled, continuous wave "green" Nd:YAG laser and a continuous wave "red" diode laser provide appropriate light for exciting the CAIS samples. Specially designed, flexible fiber-optic cables conduct the light from the laser to the sample mounted in the sample holder and return wavelength shifted light from the sample back to the imaging spectrograph. The spectrograph disperses the light from the sample into individual wavelengths, which are detected by the CCD detection system. The intensities of the individual wavelengths detected by the CCD are analyzed by the PC computer system, which displays the Raman spectrum of the sample. The spectrum is also printed on a laser printer.

During RRS operations, personnel at the glovebox will interrogate each unlabelled CAIS ampule or bottle individually with the Raman spectrophotometer. The ampule or bottle will be interrogated by inserting it into a fixed position holder to which the fiber optic probes are attached. The glovebox personnel will then direct the Raman system operator to record the Raman spectrum of the sample. The operator will provide a preliminary assessment of the spectrum and, as needed, collect more spectra to enable the segregation of the CAIS contents. Ampule or bottle orientations in the fixed position holder may be varied, or different laser excitation wavelengths may be used to maximize signal-to-noise ratios in the Raman spectra. Once the identity of the CAIS contents is established, glovebox operators will mark the ampule or bottle with a unique identification number and place the ampule or bottle in a color coded Fiber can. Ampules and bottles will be segregated into groups of chemical agent samples requiring neutralization in the RRS reactor or industrial chemicals requiring packaging in accordance with regulatory requirements for shipment to an approved hazardous waste treatment, storage, and disposal facility.

The RRS Raman system and ancillary equipment will be operated by personnel with specialized training in Raman spectroscopy, Raman spectrophotometer operations, and applications to the RRS.

2-3 DATA COLLECTION

During RRS operations, data collected for each unlabelled CAIS sample will include the CAIS sample number, physical appearance, and instrument operating parameters. Glovebox operators will relay the CAIS sample number and physical appearance data to the data recorder. Physical characteristics to be recorded for liquid samples will include coloration, opacity, presence of phase boundaries, and presence of precipitated solids. As described in paragraph 2-2, Raman spectra of the CAIS samples may be collected with different orientations of the samples in the sample holders or with different wavelengths of laser light. Instrument operating parameters recorded by the Raman system operator will include laser type used, laser excitation wavelength, and spectrum acquisition time. The Raman system operator will also record any special adjustments made to the Raman system to enhance data collection.

2-4 DATA ANALYSIS

Raman spectra will be examined by the Raman system operator to establish the identity of each CAIS sample. The primary method of identification will be the comparison of recorded spectra to laboratory reference spectra. In cases where laboratory spectra are not available, the sample spectrum will be interpreted by direct interpretation or comparison with test data recorded at DCD and ERDEC. The method and rationale for the identification will be recorded for each sample. For complex spectra that cannot be interpreted rapidly, a field decision will be made to return the sample to storage and/or retain the sample in the glovebox until a more complete interpretation of spectral data can be made for the sample.